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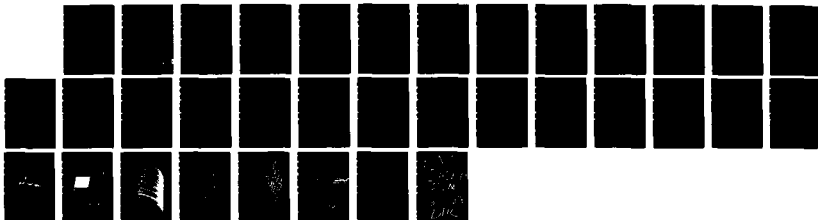
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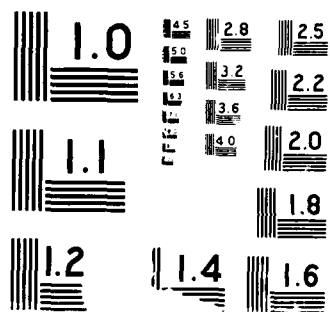
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Applications of Charge-Transfer Devices in Spectroscopy

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Patrick M. Epperson, Jonathan V. Sweedler, Robert B. Bilhorn,

Gary R. Sims, and M. Bonner Denton

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Department of Chemistry
University of Arizona
Tucson, Arizona 85721

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P.M. Epperson, J.V. Sweedler, R.B. Bilhorn,
G.R. Sims, and M.B. Denton

Department of Chemistry
University of Arizona
Tucson, AZ 85721

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ABSTRACT

This article is the second part of a discussion of the use of charge transfer devices (CTDs) in spectroscopy. The first paper discusses the operation and characteristics of these detectors, whereas this paper focuses on the spectroscopic applications of CTDs. A brief history of the development of these detectors and their application in scientific imaging is presented. The use of CTDs in spectroscopy is illustrated by four applications in challenging areas of UV-visible spectroscopy.

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Applications of Charge-Transfer Devices in Spectroscopy

Patrick M. Epperson, Jonathan V. Sweedler, Robert B. Bilhorn,
Gary R. Sims, and M. Bonner Denton

Department of Chemistry
University of Arizona
Tucson, AZ 85721

Development of charge-transfer device (CTD) detectors

Charge-transfer device (CTD) detectors consist of two closely related silicon integrated circuits: the charge-coupled device (CCD) invented in 1970 and the charge-injection device (CID) invented in 1973. Initially, several applications were proposed for these integrated circuits, including use as shift registers, logic and memory devices, electronic delay lines, and imaging detectors. The last application has so dominated the design and use of CTDs that they are among the most common electronic imaging detectors manufactured today.

The early advancement of CTD technology was driven by two different groups with contrasting needs. The first group, composed of electronic manufacturing companies such as AT&T, RCA, Fairchild, GE, Phillips, Texas Instruments, and Westinghouse, supported the early development of CTDs in an effort to design and manufacture solid state television cameras. This work resulted in the commercial manufacturing of CTDs for surveillance, robotics, and home video cameras.

The second group was led by astronomers, physicists, and engineers who needed a more sensitive and photometrically accurate detector than photographic film (1). These researchers convinced NASA and NSF to fund the development of specialized CTDs for use in space probes, satellites, and astronomical observatories. This work resulted in the first CTDs designed especially for scientific imaging as well as the furthering of the fundamental understanding of the principles of CTD imagers. This group of scientists and engineers was also responsible for the design and construction of the first "scientific" CTD camera systems. A CTD camera system used for scientific applications differs significantly from an ordinary video camera system in several ways: the rate of image digitization is comparatively slow to allow for digitization of charge

packets from 12 to 16 bits of precision; the detector is cooled to reduce dark current; and special signal conditioning circuits are employed to reduce detector noise.

Currently, there is a wide range of CTD detectors with differing operating requirements, electro-optical characteristics and formats available from a number of manufacturers. CTD detectors can have peak quantum efficiencies over 80%, a high responsivity from the soft X-ray to the near-infrared regions, dark count rates which allow integration times of many hours, and read noises several orders of magnitude lower than commercially available photodiode arrays. Readers interested in the architecture, operating methods, characteristics and the electro-optical performance of these detectors are referred to the first article in this two-part series (2).

Applications of CCDs and CIDs in Scientific Imaging

The most widespread scientific use of one class of CTDs, the CCD, is in the field of astronomy. Almost every major ground based optical telescope uses CCDs for astronomical imaging. Additionally, several space probes, such as the Giotto spacecraft sent to observe comet Halley, the Galileo spacecraft to be launched to observe Jupiter, and the Hubble Space Telescope to be launched into earth orbit by the Space Shuttle, use CCDs for optical imaging. Satellite imaging of the earth is another common application for both civilian and defense purposes. Military surveillance satellites with CCD detectors are publicly reported to be capable of identifying objects as small as 1.5 meters in diameter (3).

As the availability of CCDs increased and the results of their use in astronomy were recognized, researchers from other fields evaluated CCDs for use

in a variety of scientific imaging applications. The growth in the use of scientific CCD detector systems since 1982 was especially rapid due to the advances in CCD detectors, the commercial availability of scientific CCD camera systems, and the decrease in cost of computer memory necessary for processing large image data arrays.

The sensitivity, spatial resolution, wide spectral responsivity, and large dynamic range of scientific CCD camera systems make them ideal tools for increasing our ability to record and measure light. Although the majority of CCD applications are in the visible spectral region, select CCDs may be used to directly image anywhere in the near-infrared to X-ray spectral regions. CCDs are also used for the indirect detection of high energy electrons and photons. Indirect detection is done by converting the energy of the electron or photon into visible light with a scintillator or photocathode. The resultant visible photons are subsequently detected by the CCD. A sampling of recent scientific imaging applications of CCDs includes fluorescence microscopy of cellular components (4), high-resolution x-ray tomography (5), underwater imaging of the ocean floor (6), and imaging of protein crystal diffraction patterns (7).

Even though CIDs and CCDs are closely related detectors, the use of CIDs in scientific imaging is not nearly as extensive as that of CCDs. Nevertheless, the CID's high resistance to blooming, ability to pseudo-randomly access detector elements, good UV quantum efficiency, and ability to non-destructively read photogenerated charge, give it unique imaging capabilities not found in CCDs. The most successful scientific imaging use of CIDs is for viewing scenes with high light levels and wide variation of feature intensities as in solar astronomy (8) and star tracking (9).

Applications of CTDs in Spectroscopy

The use of CTDs as detectors for spectroscopy is also increasing, albeit at a much slower pace than that found in imaging applications. In part, this gradual acceptance of CTDs is due to the difficulties in designing optical systems that are properly matched to the capabilities of CTD detectors. The most significant instrumental challenge is the design of spectrometers that fully utilize the large number of detector elements in CTD array detectors. In imaging applications, replacement of a piece of photographic film or a vacuum tube television camera with a CTD is straight-forward. However, in spectroscopic applications, the best method of replacing single channel detectors with these one- and two-dimensional CTD detectors is not always clear. As challenging as the optical problems are, CCDs and CIDs are making their way into spectroscopic instrumentation.

Applications of CCDs in Spectroscopy

The earliest use of a CCD for spectroscopy was the evaluation of a 1728 element linear CCD for low-resolution molecular absorption spectroscopy by Ratzlaff and Paul in 1979 (10). Although this work demonstrated that linear CCDs are an acceptable detector for molecular absorption spectroscopy, these early CCDs never became popular in absorption spectroscopy because they did not offer significant advantages over other silicon multichannel detectors when measuring relatively high light levels. At high light levels the dominant source of noise is usually either source drift or photon shot noise, in which case the low-detector noise of a CCD is irrelevant.

The majority of early spectroscopic applications of CCDs concentrated on areas of UV-visible spectroscopy that are starved for photons. Not surprisingly, astronomers were the first to use CCDs for low-light level spectroscopy. Early applications of CCDs for astronomical spectroscopy include work done with conventional dispersive spectrographs (11,12) and echelle spectrographs (13). An interesting spectroscopic and imaging application of a two-dimensional CCD is the recording of the plasma torus of Jupiter in narrow spectral regions with a Fabry-Perot imaging spectrometer (14).

The wide range of analytical spectroscopic applications using a CCD is illustrated by focusing on recent applications in three challenging areas of UV-visible spectroscopy. Several unconventional spectrometer designs and CCD operational modes are described.

Low Light Level Spectroscopy with a CCD Detector

Until recently, the cooled photon counting photomultiplier (PMT) was the detector of choice in spectroscopy for measuring low light levels in spite of it being a single channel detector with a relatively poor quantum efficiency. Various intensified multichannel detectors have been evaluated for replacing PMTs, and although they offer a significant multichannel advantage, intensified array detectors suffer from a generally poor quantum efficiency from the intensifier photocathode.

The ability to integrate for hours, the high visible and near-infrared quantum efficiency, and the low detector noise of the CCD make it an ideal detector for long integration, low light level measurements. Preliminary work in our laboratories employing a 512 by 320 element CCD for molecular fluorescence measurements has resulted in the lowest reported detection limit of anthracene of 1 part-per-trillion at a S/N of 2 (15). In spite of the use of a

relatively weak 35 watt deuterium lamp for fluorescence excitation in this work, the detection limit is an order of magnitude lower than a system employing a high power (and expensive) tunable dye laser for fluorescence excitation (16). A spectrum of anthracene at a concentration close to the detection limit is shown in Figure 1.

The high sensitivity of CCDs is increasing the analytical utility of Raman spectroscopy by lowering detection limits and decreasing the time needed to acquire spectra. For example, Murray and Dierker employed a CCD detector system for the unenhanced detection of monolayers of organic adsorbates on surfaces (17). They report an impressive signal-to-noise-ratio of 15 when measuring monolayer coverage of cadmium stearate Langmuir-Blodgett films deposited on glass and silicon substrates.

A direct comparison by Pemberton and Sobocinski (18) of the Raman spectra obtained with a PMT and CCD for equal exposure times illustrates the improvement possible when a cooled photon-counting PMT is replaced by a 576 by 384 element CCD scientific camera system (Figure 2). The CCD is placed at the exit port of a double monochromator and oriented so that the dispersion direction is the long axis of the CCD. When using the CCD, the only modifications to the spectrometer are the removal of the exit slits and the widening of the center slits of the double monochromator. The technique of binning photogenerated charge (19) from adjacent detector elements is used to combine photogenerated charge packets from 40 detector elements into a single charge packet. Because of the CCD's high quantum efficiency around the laser excitation wavelength of 514.5 nm and the simultaneous integration of charge over 288 wavelength channels (576 columns binned two-fold in the direction of wavelength dispersion), the signal-to-noise-ratio of the spectrum obtained with the CCD is approximately 14 fold better than

the spectrum obtained with the PMT for a 5 minute spectral acquisition time. For an equal S/N, this 14 fold increase in sensitivity translates into a decrease in integration time ranging between 14 to 196 fold, depending on whether the measurement is detector or photon shot noise limited.

The improvement in detector sensitivity is promising for increasing the analytical usefulness of Raman spectroscopy. Such improvements should result in lower detection limits, more rapid analysis, and the opportunity to use lower power, less expensive lasers. Decrease in analysis time makes the measurement less prone to source drift and sample photo-decomposition. Additionally, because CCDs have a broad spectral response extending into the near-infrared, fewer detector restrictions on the choice of laser wavelength for Raman excitation exist than when using PMTs or intensified multichannel detectors which employ photocathodes in the first intensification stage. The ability to select a longer excitation wavelength can be advantageous in reducing luminescence background from complex samples.

Time Resolved Spectroscopy with a CCD Operated in a "Spectral Framing Mode"

A CCD operated in a "spectral framing" readout mode can greatly improve the sensitivity of time-resolved spectroscopy for spectral measurements in the microsecond and slower time domain. This special readout mode uses one dimension of the CCD to record wavelength information and the other dimension to record temporal information (20,21).

Spectral framing uses the parallel transfer of photogenerated charge in a CCD to capture and store time-resolved spectra. The CCD is placed at the focal plane of a flat-field spectrometer as shown in Figure 3. An opaque mask covers the entire imaging portion of the CCD except for the last row. Light from the

temporal event is collected and dispersed by the grating across the unmasked row of the CCD. The spectral coverage is determined by the width of the CCD and the linear dispersion of the spectrometer.

Initially, the CCD is cleared of all charge. After the event is initiated, photons are absorbed and converted into electrons in the unmasked row. These electrons are integrated during a single "frame" time and make up one spectral image. At the end of the frame time, the CCD parallel gates are clocked and photogenerated charge in every row of the CCD is shifted up by one row toward the serial register. This results in the shifting of charge in the unmasked row to the adjacent masked row of the CCD. A new spectral image is then acquired during the next frame time in the unmasked row. The process of integrating and shifting is repeated until each row in the masked portion of the CCD is filled with a spectrum. The unmasked portion of the CCD acts as a linear detector array, whereas the masked portion acts as a 2-dimensional analog shift register for the temporary storage of time-resolved spectra.

At the completion of the experiment, each row in the masked portion holds a spectrum acquired in a unique time period or frame. This stored analog image is shifted out of the CCD in a normal fashion and converted to a digital image. The time-resolved spectra of an xenon-flash lamp taken with one spectrum every 6 microseconds are shown in Figure 4 (22).

The processes of spectral image acquisition and readout are temporally isolated in spectral framing by the masked portion of the CCD which acts as a virtually noiseless analog storage register. Because the CCD is cooled to -135 °C, spectral images can be stored for many minutes without degradation by dark current. The low dark current relaxes the time requirements on both the slowest rate at which spectra are acquired and the rate of image digitization.

The rate of spectrum acquisition is determined by the parallel clocking rate of the CCD. The maximum rate is determined by the ability of the CCD to efficiently transfer charge in the imaging portion of the CCD and is approximately one microsecond per transfer for most CCDs. Because the clocking of the parallel phases of the CCD is under computer control, linear and non-linear time bases are possible. For example, an exponentially increasing time base is useful to maintain a constant signal intensity per spectrum for an exponentially decaying spectral event.

Spectral framing has a number of advantages compared to mechanical rapid scanning spectrophotometers. The spectral framing instrument is more sensitive than a single channel instrument because of the CCDs relatively high QE, low noise, and ability to integrate simultaneously all wavelengths. The spectral framing spectrometer is inherently more reliable than rapid scanning spectrometers because it achieves time resolution by the electrostatic shifting of charge in a single crystal silicon lattice.

Spatially Resolved Spectroscopic Measurements with a CCD detector

The high spatial resolution of a CCD allows it to easily analyze light transmitted through or reflected by spatially heterogeneous samples. For example, the single-beam instrument shown in Figure 5 was used to accurately measure absorbances from spatially non-uniform, optically dense metal-phthalocyanine films (23). Metal-phthalocyanine thin films, formed by the sublimation of metal-phthalocyanine onto optically transparent polyester films, are being investigated for use in photovoltaic cells, chemical sensors, and photocopiers. Different sublimation conditions cause the formation of different crystalline phases of the phthalocyanine films and these different phases show important

variations in their absorption spectra and photovoltaic behavior (24). Some of these crystalline phases result in comparatively thick and therefore, optically dense films.

Generally, absorption measurements of thin films are easily made; however, in the case of these optically dense films, accurate absorption measurements are impossible with conventional absorption spectrophotometers. The first difficulty in measuring the spectra of these films is that the absorbances range from 0.2 to 5 absorbance units over a 300 nm interval in the visible region. Most commercial spectrophotometers are optimized to measure very small absorbance differences and are not suited to handling such a wide dynamic range of photon fluxes. When measuring wavelength regions of high absorbance, stray light from weakly absorbed wavelengths causes serious errors in single monochromator spectrophotometers. Additionally, at wavelengths of high absorbance, only a small fraction of the incident photons pass through the sample; thus the signal is weak and difficult to measure above the noise of the detector.

A second difficulty arises from the spatial non-uniformity of these thin films. The sublimation process is not perfect; often the organic film fails to adhere to the polyester substrate in small areas resulting in pinhole defects. The transparency of such randomly spaced pinhole defects can easily be the dominant source of transmitted light, making the measurement of the true absorbance of the metal-phthalocyanine film impossible with conventional techniques.

These difficulties are overcome by using a CCD as an imaging absorption spectrometer. The thin film is attached to the exit slit of the double monochromator and the light transmitted through the film is focused onto the 512 by 320 element CCD. An absorbance spectrum is acquired by first measuring the intensity of light transmitted through the thin film sample as a function of

wavelength. The measurements are then repeated with an uncoated sheet of polyester serving as the reference blank.

The double monochromator provides the high stray light rejection necessary when measuring samples with widely varying absorbance values with a broad band source of light. The CCD imager provides both the sensitivity for measuring the small fraction of light that is transmitted at absorbances as high as 5 absorbance units, and the ability to spatially discriminate against areas of the film that contain defects.

Applications of CIDs in Plasma Emission Spectroscopy

Elemental analysis of complex samples by plasma emission spectroscopy is inherently capable of generating a vast amount of spectral information over a wide dynamic range. Samples may contain 20 or more elements of interest in concentrations ranging from the high part-per-thousand to low part-per-billion. Each element emits light at many different wavelengths in the vacuum UV to near IR spectral region. The intensities of spectral lines of analytical interest typically vary by six or more orders of magnitude due to the differences in transition probabilities, and the population differences of various quantum states. The analyte emission lines are superimposed upon a complex plasma background of emission lines and bands from the carrier gas and analyte solvent. The measurement process is further complicated by analyte and background emission intensities that are dependent upon a number of plasma and nebulizer conditions that can drift during a measurement.

An ideal instrument for atomic emission spectroscopy simultaneously measures as many emission lines and as much background as necessary to quantitate

each element of interest in a complex sample. For simple sample matrices, the probability of a spectral interference is low, and the measurement of one emission line and its surrounding background for each element may be sufficient. For complex samples, the probability of interfering spectral features is greater, and an emission line from one element may suffer an interference from nearby emission lines of other elements. In general, it is desirable in complex samples to measure several emission lines and associated background regions for each element to reduce the chance of incorrect analyses due to matrix interferences.

An echelle spectrometer employing a two-dimensional CID array detector is being employed for direct current plasma atomic emission spectroscopy (25,26). Two-dimensional CID array detectors provide the necessary number of resolution elements for measuring hundreds of emission lines and surrounding background, but the detector elements are arranged in a format that is optically incompatible with conventional spectrometers. Simple prism or grating instruments disperse a spectrum across a curved focal plane that is quite large compared to the dimensions of the average CID detector. However, the echelle spectrometer provides a nearly ideal optical format for a two-dimensional array detector (27).

The CID echelle spectrometers use an echelle grating for high dispersion and a quartz prism as a cross-disperser to separate grating orders. A telescope reduces the two-dimensional spectral image to a size compatible with currently available two-dimensional CIDs. The CID-echelle spectrometer monitors the majority of the UV-visible spectral region containing the analytically important emission lines. A portion of the atomic emission spectrum from a sample con-

taining 1 ppm Fe in a 1000 ppm Gd matrix is shown in Figure 6. The high resolution of the echelle spectrometer allows the quantitation of Fe even in the midst of a forest of Gd emission lines. The presence of the Gd matrix degrades the detection limit of Fe from 1 ppb to only 2 ppb.

The CID's ability to perform non-destructive readouts of photogenerated charge packets enables the detector to monitor the integrated photogenerated charge from hundreds of spectral lines. Non-destructive readout of charge allows the computer system to choose the optimum integration period for each spectral line. Intense lines are digitized early in an exposure so as to record their intensity before they saturate a detector element, while weak spectral lines are recorded toward the end of an exposure so as to maximize the integration time. Because the detection of photogenerated charge by non-destructive readout leaves the image undisturbed, the proper exposure time for each emission line can be determined during the analysis without any prior knowledge of the sample composition. If a spectral line is not intense enough when first measured non-destructively, the system returns to measure this line later in the analysis when the signal has integrated to a higher, more readily detectable level.

The ability of the CID-echelle spectrometer to simultaneously measure both the analyte emission lines and the background greatly enhances its ability to perform background corrections. The background correction procedure measures and digitally stores the spectral background around the location of the analyte emission line for both the blank and the sample. The blank background is then digitally subtracted from the sample background (Figure 7). The blank corrected image is used for determining the emission intensities and sample concentrations. This method of background subtraction results in a very "clean"

correction. Because the spectrometer has no moving parts, the blank and sample images are subtracted from each other with precise spatial registration. Because of the large number of channels present and the integrating capability of the CID, one does not have to trade time spent measuring the analyte line for time spent measuring background.

The ability to conveniently choose wavelength regions is another important aspect of the instrument. For quantitative analysis, only selected portions of the spectral image need to be monitored. This allows more time for interrogating spectral lines of interest, while ignoring portions of the spectral image that do not contain useful information. The choice of spectral lines to be monitored is determined by the needs of the analysis, and includes such factors as the elements of interest, their concentrations, and possible interferences. The most intense resonance lines of elements generally give the best sensitivity at trace concentration levels. The less intense lines resulting from non-resonance and ionic transitions are used for elements found at high concentrations to reduce errors due to self absorption. When possible, multiple spectral lines are used for each element to enhance precision.

Future of CTDs in analytical spectroscopy

The use of CTDs for scientific imaging and spectroscopy is just beginning. The growth in use will be partially driven by the commercial availability of CTD instrumentation as well as computer hardware and software capable of processing and storing large images. Prior to 1980, two-dimensional scientific grade CTD detector systems were too costly for almost all groups except large observatories and a few government laboratories. Advances in silicon integrated-circuit fabrication have decreased the cost of CTDs as well as the associated

computer hardware. The cost of available CTD detectors varies widely from \$100 for 3500 element linear arrays, \$2000 for one-hundred-thousand element arrays, to over \$50,000 for prototype detectors. Complete commercially available scientific CTD detector systems range in price from \$20,000 for a thermoelectrically cooled detector to \$50,000 for a liquid nitrogen cooled system with a complete image processing computer system, making them competitive with other imaging detector systems such as vidicons and photodiode arrays (28).

Many early spectroscopic applications of CTDs were implemented to improve the sensitivity of measurements that were normally done with single channel scanning instruments. It is expected that research will continue in replacing single channel detectors with CTDs in light limited areas of spectroscopy such as Raman and luminescence. Additionally, CTDs should offer improvements in spectroscopic measurements that become light limited because of small sample size or limited observation time, such as micro-HPLC UV-visible absorbance detection.

An important area of work related to the use of CTDs is the development of intelligent software operating systems that efficiently extract meaningful information from the massive amounts of data generated with large arrays. In certain areas of spectroscopy, notably atomic emission spectroscopy, sufficiently intelligent software can take advantage of the tremendous amount of chemical information contained in a high-resolution emission spectrum. Because the instrument is not detector limited, the dedication of a number of the CTD detector elements to instrument diagnostics is possible. In the example of the echelle-CID spectrometer discussed earlier, work is being done to monitor not only analyte lines and surrounding background, but also key plasma emission

lines that provide diagnostic information about the nebulizer-source performance. This "intelligent spectrometer" (25,26,29) would measure the analyte concentrations and at the same time monitor the spectrometer system's performance. Information gleaned from the background emission could be used to notify the operator of changes in solvent, sample matrix, nebulizer efficiency, or plasma temperature.

Future applications of CTDs will arise as scientists ask more complex and detailed questions about physical systems. Researchers are often constrained by instrumental limitations of sensitivity or time to measuring only a few parameters of a physical system. A sensitive multichannel CTD detector coupled with the right optical and computer systems serves to relax these constraints and allow scientists to simultaneously measure several parameters. The broad objective of research into CTD systems is to develop instrumentation that does not limit a scientist's ability to gather all of the spectral, spatial, and temporal data of a physical system.

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Figure Captions:

1. Fluorescence spectrum of 1×10^{-11} M anthracene in ethanol measured by a two-dimensional CCD. This spectrum is result of 10 second integration of sample minus 10 second integration of ethanol blank. Excitation source is a 35 watt deuterium lamp filtered with a 250 nm bandpass filter. The CCD is placed at the focal plane of a 200 groove/mm concave holographic grating spectrograph.
2. Raman spectra of 5×10^{-3} M pyridine in water excited at 514.5 nm by a 300 milliwatt argon ion laser. CCD -- 576 by 384 element Thomson-CSF CCD controlled by a Photometrics Model CH181 detector system operated at -135 C with 5 minute integration. PMT -- RCA C31034 GaAs photocathode PMT and SPEX Data-mate photon counting unit thermoelectrically cooled to -25C with a 5 minute scan time. (Published with permission, J. E. Pemberton and R. L. Sobocinski, Department of Chemistry, University of Arizona.)
3. Spectral framing readout mode of a CCD for time-resolved spectroscopy. The CCD is placed at the focal plane of spectrograph. The spectrum is dispersed across the unmasked row of the CCD. Time resolved spectra are captured and stored by the parallel transfer of the photogenerated electrons in the unmasked row to the masked portion of the CCD. After all rows of the CCD are filled with spectra, charge in the CCD is read out in a normal fashion and converted to a two-dimensional image. The image is the time (vertical) versus wavelength (horizontal) output of the spectral event.

4. Time-resolved spectra of xenon flash lamp acquired by a CCD operated in the spectral framing mode. A 320 point spectrum is obtained every 6 microseconds, although only a portion of the data is displayed in this plot. (published with permission from reference 22.)
5. Spectrometer for measuring absorbance of optically dense thin films. The thin film is placed on the exit slit of the double-monochromator. Monochromatic light transmitted through thin film is imaged onto the CCD detector for .1 to 20 second integration periods depending on absorbance of film.
6. Atomic emission echellogram of 1 ppm Fe in a 1000 ppm Gd matrix. The plot covers a small section of 7 orders of the echellogram at approximately 0.04 nm per detector element. The high resolution of the echelle spectrometer allows the determination of Fe in the midst of a complex emission spectrum.
7. Background subtraction technique of CID-echelle spectrometer.
 - a. Portion of an atomic emission echellogram of an Fe solution showing analytical lines with background from the plasm
 - b. Atomic emission echellogram of blank solution and plasma background.
 - c. Background subtracted echellogram showing one major and several minor Fe emission lines. (Reprinted with permission from Reference 25.)

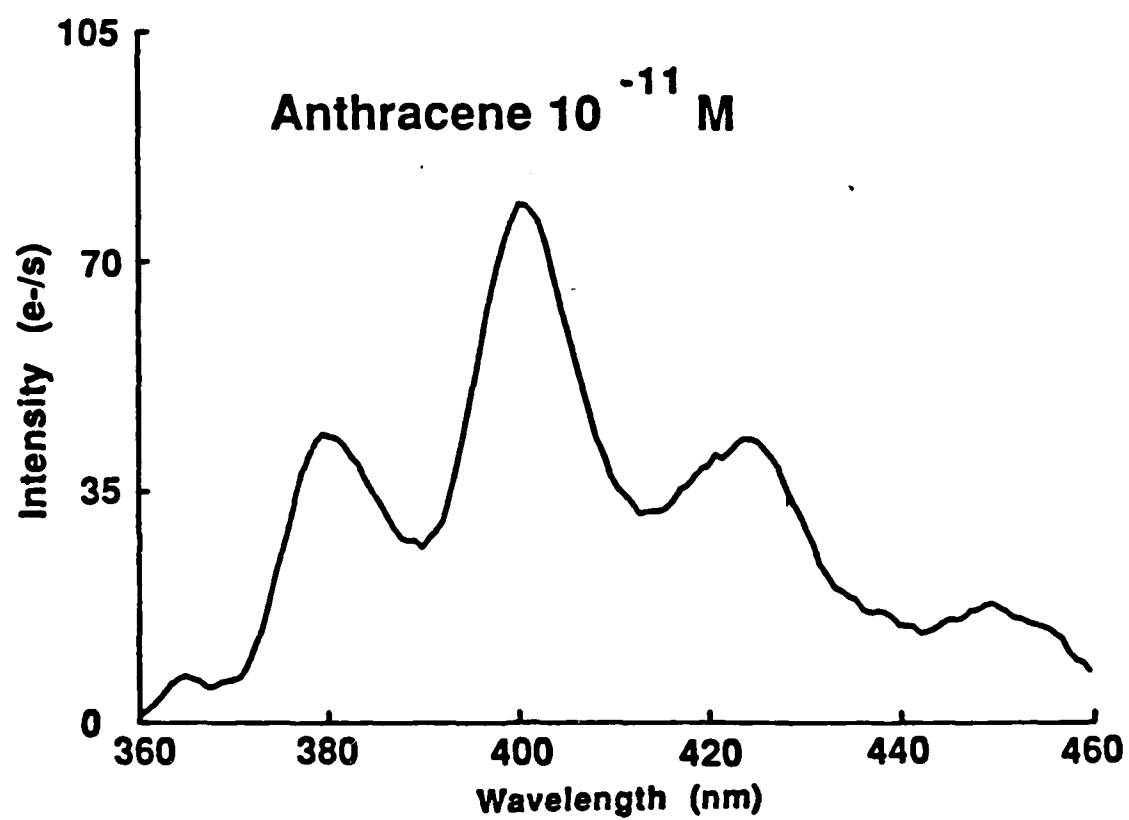


FIGURE 1

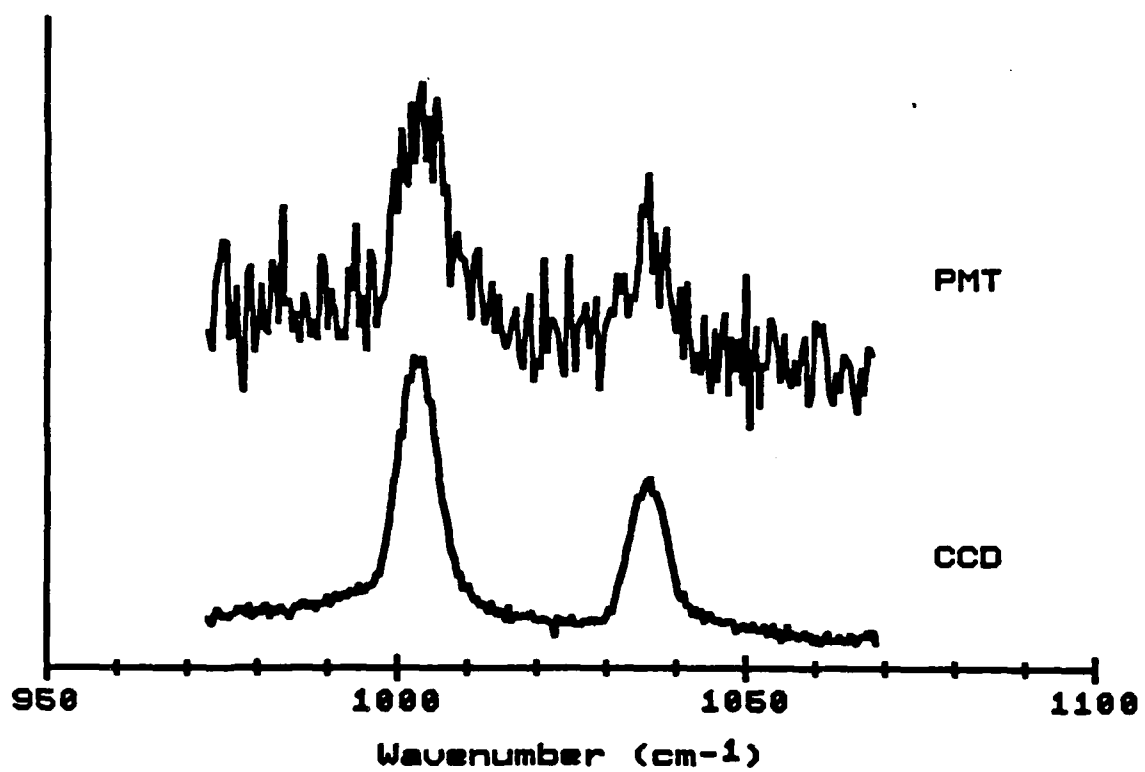


FIGURE 2

Spectral Framing CCD

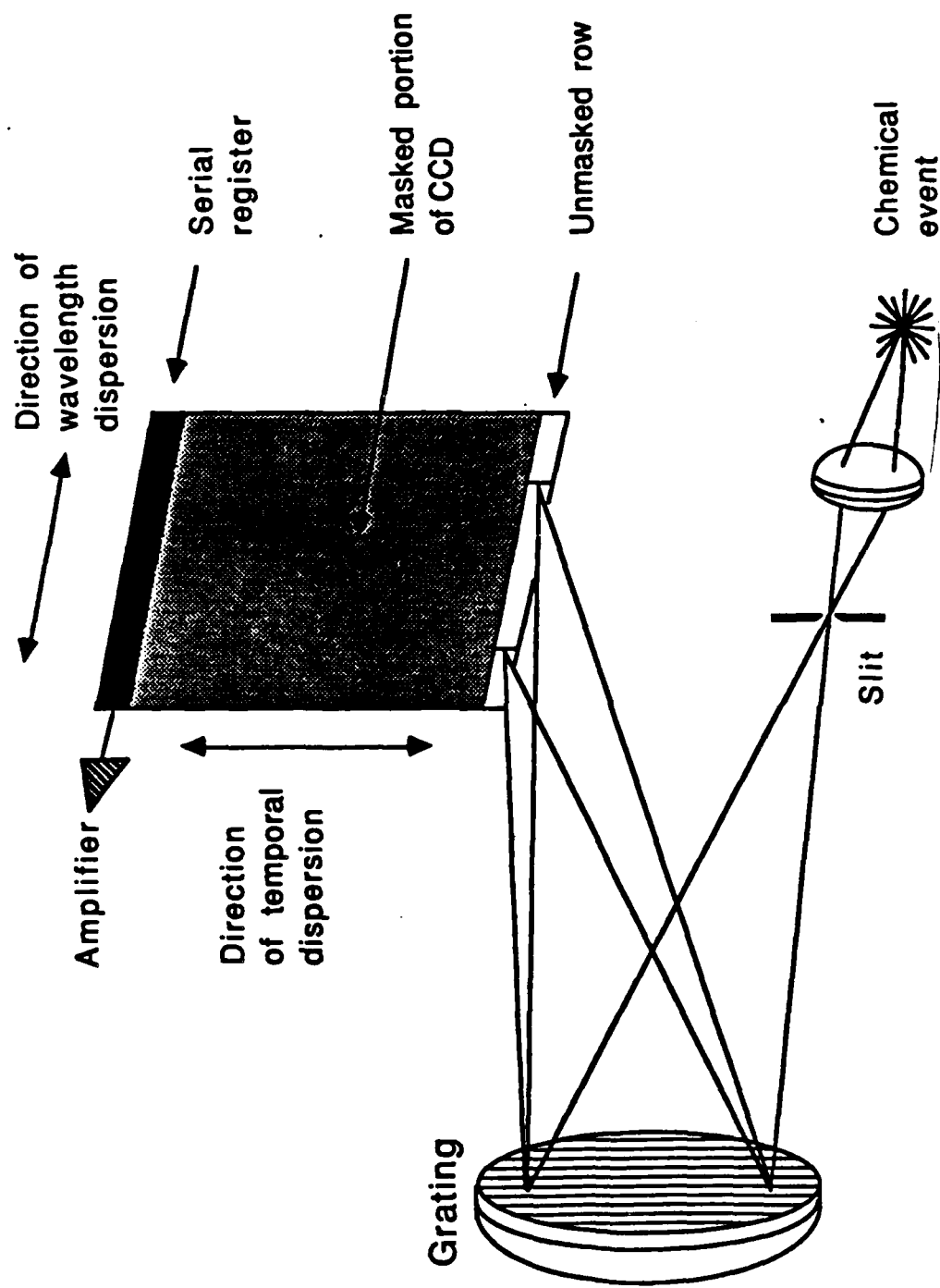
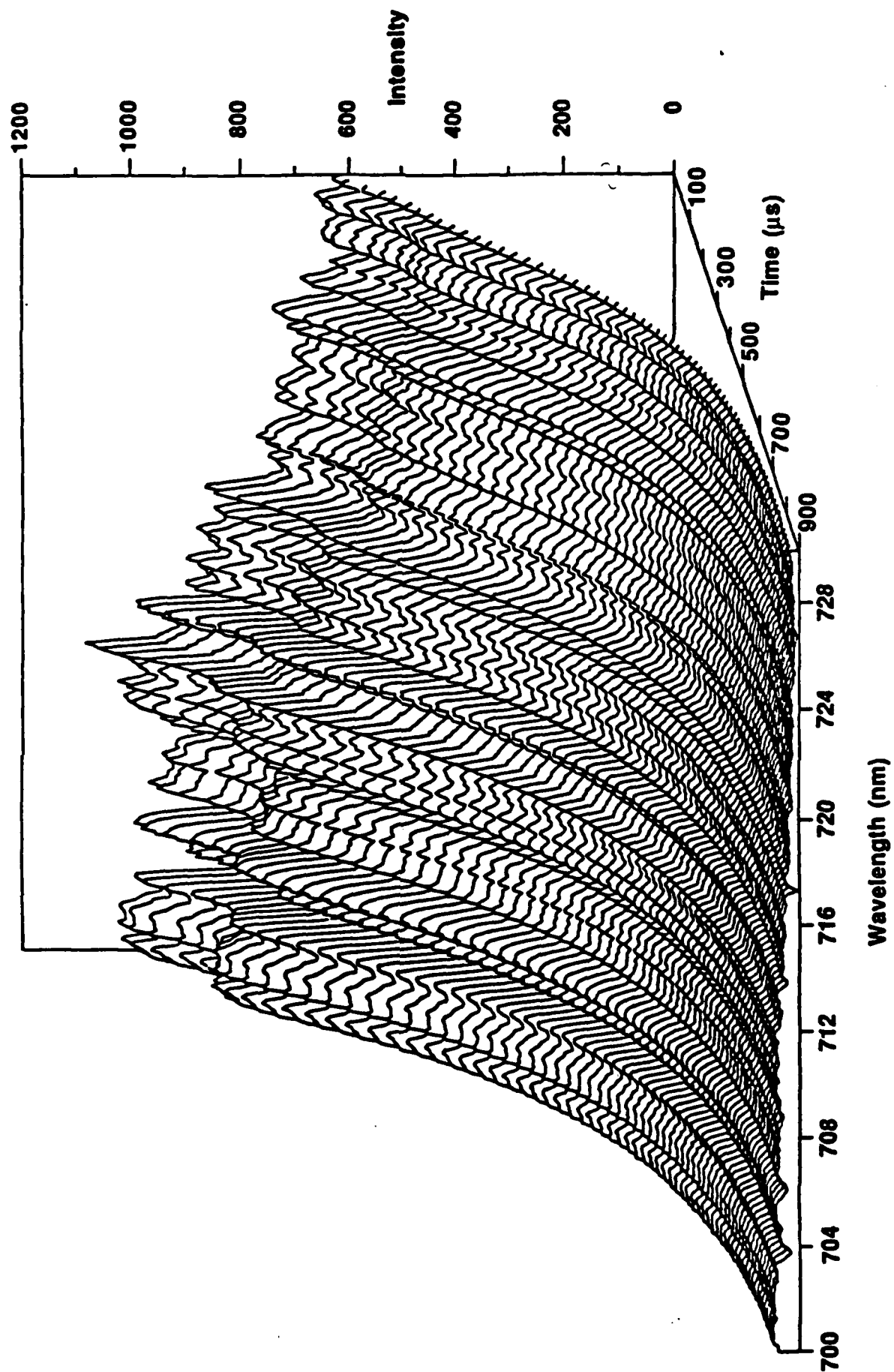


FIGURE 3



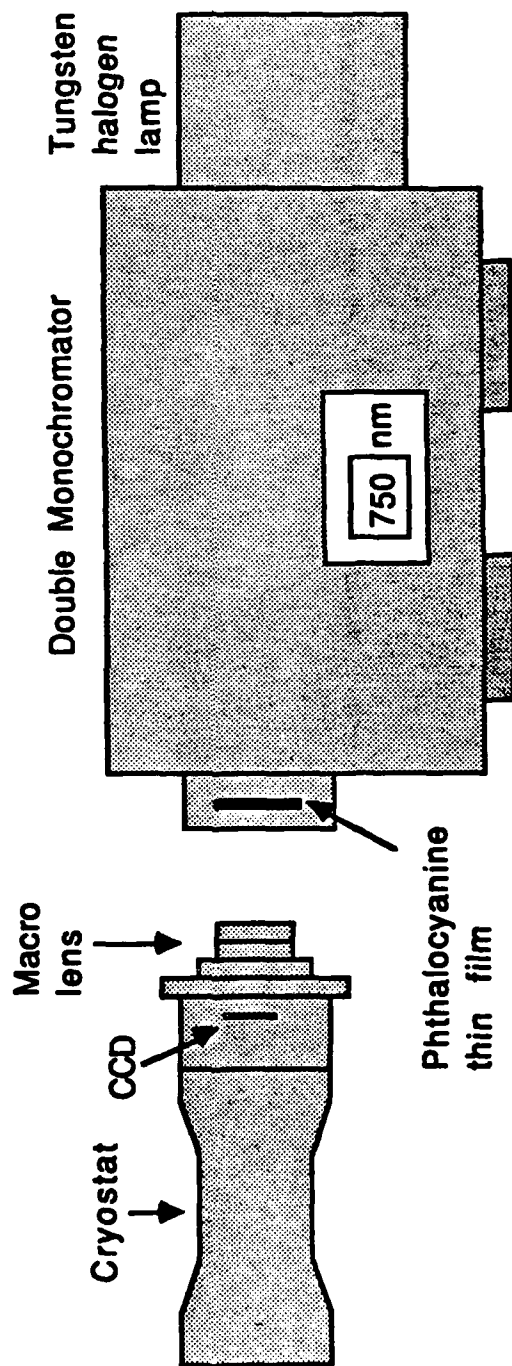


FIGURE 5

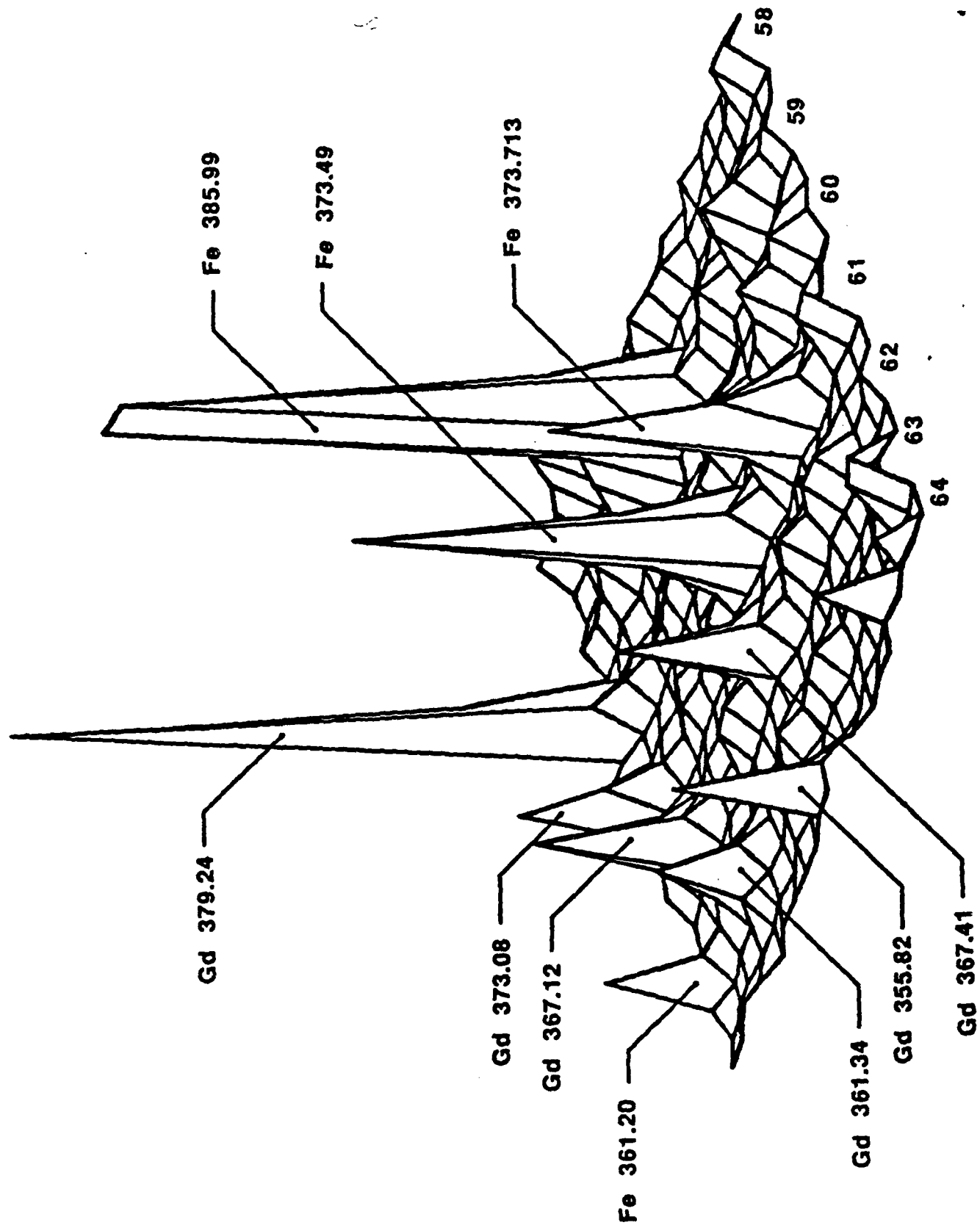


FIGURE 6

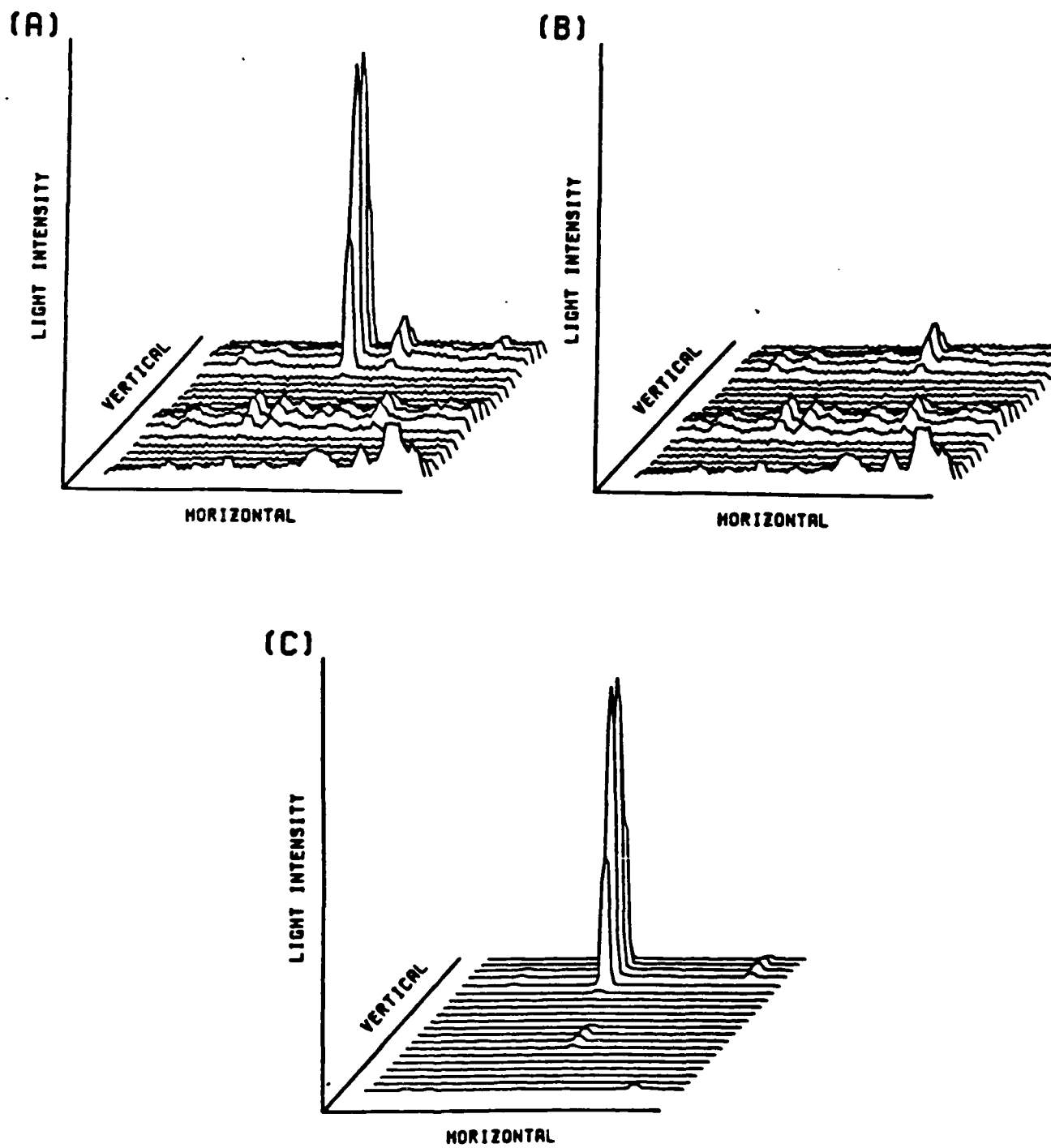


FIGURE 7

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